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Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office  
Le Président de l'Office européen des brevets  
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Biodegradable polymer material and its use to gelatinise starch

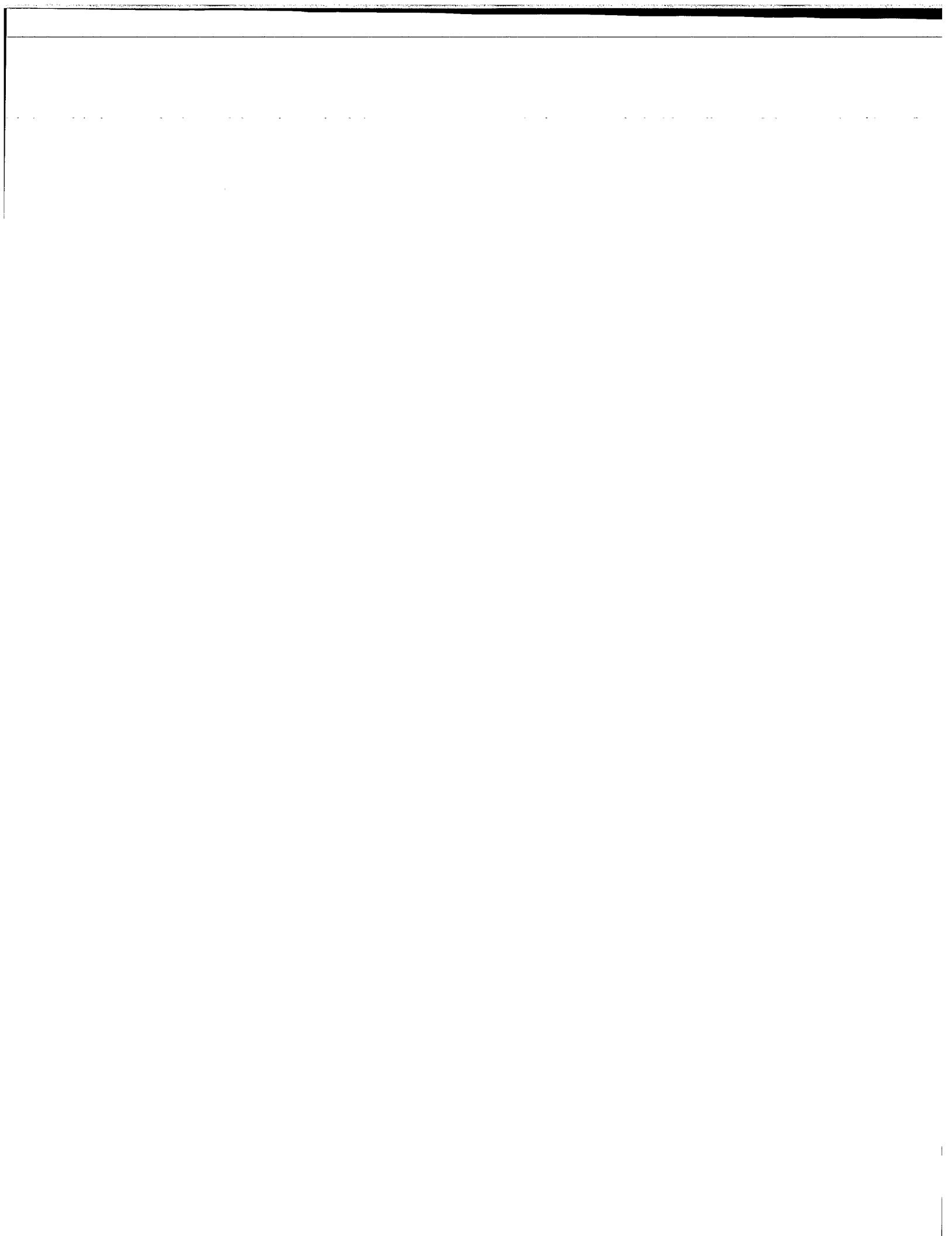
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Title: Biodegradable polymer material and its use to gelatinise starch

The invention relates to a starch formulation that promotes gelatinisation of starch by means of a thermo mechanical treatment.

Thermoplastic starch has proved suitable as a material for the production of biodegradable moulded products, such as packaging material.

5 Apart from biodegradability, starch has the advantage that it is available from an inexhaustible source, in contrast to more common materials, such as those based on fossil hydrocarbons.

Starch has to be rendered thermoplastic for processing to moulded products for this purpose the crystal structure of starch must be disrupted by

10 gelatinisation. A thermal treatment in the presence of water is usually needed for gelatinisation. Gelatinisation is often combined with a thermo mechanical treatment. Extrusion is a suitable process for this. A plasticiser is needed in the thermoplastic processing of starch. Water itself acts as a plasticiser, but usually supplementary plasticisers, such as glycerol or urea, are used for

15 efficient process control.

A disadvantage of the known extrusion methods is that relatively high temperatures, above 120 °C, and large amounts of plasticiser (for instance 25 % (m/m), based on the dry starch) are needed for the continuous thermo mechanical treatment of the starch, which has the result that the

20 mechanical properties decrease with increasing plasticiser concentration.

Moreover, the processing of starch is more difficult, and in particular slower, than the processing of the polyolefins usually used, such as PE. The production rate of an extruder is 2.5 times lower with starch than with PE.

25 Another disadvantage of these thermoplastic starch products is their high sensitivity to water. Consequently, they cannot be used as packaging material for many applications.

In WO 99/02599 it is proposed to add 5 - 30 % dialdehyde starch (DAS) to starch in order to improve the water resistance of the end product formed. The dialdehyde starch applied has a high degree of oxidation (70 - 95 %) which means that all of the modified monomer units of the starch comprise 5 at least two aldehyde groups per unit.

Surprisingly, it has now been found that the addition of a carbohydrate polymer with aldehyde containing monomer units that comprise no more than one aldehyde group per monomer unit has a beneficial effect on the continuous processing of the starch. Even small amounts of monomer units 10 comprising only one aldehyde group allow a considerable lowering of the extrusion temperature and the capacity of the extruder is considerably increased. In this context it has surprisingly been found that not all aldehyde containing monomer units need to comprise two or more aldehyde groups per monomer unit, but that a smaller number of aldehyde groups in the 15 carbohydrate polymer has a beneficial effect on the processing of the starch, in the sense that the processing procedure proceeds more efficiently and with a lower energy consumption than without the addition of this particular carbohydrate polymer. Additionally, it has been found that the addition of a carbohydrate polymer containing such a relatively small number of aldehyde 20 groups to produce thermoplastic starch, allows the end product to be dimensionally stable in water. Further, the carbohydrate polymer to be used in accordance with the present invention is much cheaper when compared to materials such as dialdehyde starch (DAS). Moreover, the application of a smaller number of aldehyde groups in the carbohydrate polymer as such and 25 per aldehyde containing monomer unit, when compared to WO 99/02599, is also found to be associated with a better tensile strength (higher modulus). Consequently, a cross-linking agent (glyoxal and the like), such as is used according to WO 99/02599, is not needed in this case, which allows the process to be carried out much more efficiently and cost-effectively.

Accordingly, the present invention relates to a process for gelatinising starch and/or a starch derivative by subjecting starch and/or a starch derivative in the presence of a carbohydrate polymer to a thermo mechanical treatment, which carbohydrate polymer comprises aldehyde containing monomer units, whereby at least 1% of the aldehyde containing monomer units comprise no more than one aldehyde group per monomer unit, and the remaining aldehyde containing monomer units comprise two or more aldehyde groups per monomer unit.

Preferably, the thermo mechanical treatment is carried out continuously. Suitably, such a continuous thermo mechanical treatment is carried out by means of an extrusion process.

Preferably, at least 10 % of the aldehyde containing monomer units of the carbohydrate polymer to be used in accordance with the present invention comprises no more than one aldehyde group.

More preferably, at least 20 % of the aldehyde containing monomer units of the carbohydrate polymer to be used in accordance with the present invention comprises no more than one aldehyde group.

In practice this means that the aldehyde containing monomer units of the carbohydrate polymer to be used in accordance with the present invention comprise on average 1-3, and preferably 1-3 aldehyde groups per aldehyde containing monomer unit. Based on total number of monomer units (including non-modified units) the carbohydrate polymer to be used comprises on average 1-299, preferably 2-280, and most preferably 3-100 aldehyde groups per hundred monomer units.

The carbohydrate polymer to be used in the present invention can e.g. be derived from any carbohydrate polymer containing 1,2-dihydroxyethylene groups in its recurring monomer units. Such carbohydrate polymers include non-reducing disaccharides and oligosaccharides, such as sucrose, raffinose, trehalose and similar oligosaccharides, and polysaccharides which are 1,2-, 1,4- or 1,6-linked. Examples include  $\alpha$ -1,4-glucans (the "starch

family"),  $\beta$ -1,4-glucans (cellulose), glucomannans and galactomannans (guar and locust bean gum), (arabino) xylans (hemicellulose) and  $\beta$ -2,1 and  $\beta$ -2,6-fructans (inulin and levan). The starch-type carbohydrates, cellulose and inulin are preferred carbohydrate polymers.

5 Modifications of starch and other carbohydrate polymers can also be used as starting materials, and comprise partially hydrolysed products, as well as physical and chemical modifications, including hydroxyalkyl, carboxyalkyl and similar derivatives, as well as uronic acid analogues.

The carbohydrate polymers to be used in the invention can be  
10 obtained by subjecting a carbohydrate polymer starting material as defined here above to an oxidation treatment. In this way in monomer units of the carbohydrate polymer, the C6-hydroxy group can be converted into one aldehyde group per unit only, whereas in other (the remaining) monomer units the 1,2-dihydroxyethylene groups (e.g. in starch C2 and C3-hydroxy groups)  
15 can be converted into two aldehyde groups per unit, or the C2, C3 and C6-hydroxy groups can all three be converted into aldehyde groups.

This can suitably be established by subjecting the carbohydrate polymer to an oxidation treatment. Such oxidation treatments are as such known to the skilled person.

20 Alternatively, the aldehyde groups could be introduced into the monomer units by way of substitution. This can for instance be established by subjecting the carbohydrate polymer to a substitution treatment wherein use is made of protected aldehydes (acetals) or substituted unsaturated functionalities followed by oxidation of e.g. through hindered nitroxyl  
25 mediated oxidation. In this way modified monomer units can be obtained which comprise one aldehyde group per modified monomer unit, whereas other (the remaining) monomer units can be obtained which comprise two or more aldehyde groups per unit. Such substitution treatments include periodate oxidation in combination with the earlier mentioned methods.

Suitable carbohydrate polymers include polysaccharide esters described in US 4,749,800; US 6,265,570 B1; and US 4,801,699, which documents are herein incorporated by reference.

The carbohydrate polymers to be used in the present invention can 5 be also suitably derived from dialdehyde carbohydrate polymers by selectively oxidising one of the two aldehyde groups into a carboxyl group. Preferably, the number of carboxylic acid groups is not higher than the number of aldehyde groups per modified monomer unit.

A suitable class of such carbohydrate polymers are those described 10 in WO 00/26257, which document is herein incorporated by reference. The carbohydrate polymers described in this document have an aldehyde to carboxyl ratio of between 25/75 and 80/20, especially between 40/60 and 75/25. They contain on average 0.1-1.5, preferably 0.5-1.3 carboxyl, and 0.5-1.9, preferably 0.7-1.5 aldehyde group per oxidised 1,2-dihydroxyethylene group. 15 Per total number of monomer units (including non-modified monomer units, if any), these carbohydrate polymers contain on average 0.1-1.2, preferably 0.2-1.0 carboxyl group and 0.2-1.5, preferably 0.3-1.2 aldehyde group per monomer unit.

It should be noted, however, that as a result of the 1,2- 20 dihydroxyethylene groups being oxidised into two aldehyde groups, the vicinal diol system is cleaved between e.g. C2 and C3 in the case of starch.

Surprisingly, it has now been found that carbohydrate polymers can very attractively be used in the present invention when their vicinal diol systems have not been cleaved. The carbohydrate polymers which comprise 25 such non-cleaved vicinal diol systems are easier dissolved, stored under dry conditions, more stable under basic and oxidative conditions and display an improved processability when compared with carbohydrate polymers of which vicinal diol systems have been cleaved.

Suitable carbohydrate polymers comprising non-cleaved vicinal diol 30 systems include starch, cellulose and hemi-cellulose and galactomannans.

In the process according to the present invention the carbohydrate polymer preferably comprises starch and cellulose.

In addition to the aldehyde groups, the carbohydrate polymer may also contain other functional groups, such as hydroxyalkyl groups, cationic groups, carboxyl groups and other acid groups.

A considerable improvement in gelatinisation is already obtained when the carbohydrate polymer to be used according to the present invention is present in an amount of from 1 to 15 % (m/m), based on the dry starch. Preferably, the carbohydrate polymer is present in an amount in the range of 10 from 2 to 10 % (m/m), based on dry starch. Furthermore, it has been found that addition of small amounts of the carbohydrate polymer already improve the viscosity of the melt considerably, bringing about an improved processing of the starch. Amounts of more than 15 % (m/m) can be used, for example up to 20 % (m/m), but will result in no further significant improvement in the 15 processing of the starch. Most preferentially, 3 – 12 % (m/m) of the present carbohydrate polymer is used.

The carbohydrate polymer to be used in accordance with the present invention can have a wide range of average molecular weights, for example from 20 kD to 2000 kD. Preferably, the present carbohydrate polymer has an 20 average molecular weight in the range of from 40 kD to 1500 kD.

The starch that is gelatinised according to the present process can be any type of starch, for example originating from potatoes, maize, cassava, etc. It can also be starch with a high amylose content or, specifically, a high amylopectin content, optionally produced by recombinant organisms. Also two 25 or more types e.g. as a mixture of starch can be used. The starch can be mixed with any other naturally occurring polymer (biopolymer) that can be thermoplastically processed separately from or together with starch, such as cellulose, chitosan, alginate, other microbial or vegetable gums, pectin, gelatine, polylysine, casein or other proteins. Modified starch and modified 30 forms of the other hereinabove-mentioned naturally occurring polymers can

also be present. Preferably, the percentage of starch in the total amount of the biopolymer is at least 30 % (m/m), in particular at least 80.%(m/m).

Starch derivatives that can suitably be gelatinised with the process of the present invention include for instance cationic starch and acetylated starch. A mixture of two or more starch derivatives can be used in the process of the present invention. Also mixtures of one or more these starch derivatives and one or more of the above-mentioned types of starch can suitably be used in the present process.

Water is the most effective plasticiser for starch. The amount of water relative to starch is 5 - 80 %, that is to say 5 - 80 g water per 100 g dry starch or starch/biopolymer mixture, preferably 15 - 70 % and more preferentially 20 - 60 % (m/m).

For the long-term stability of the thermoplastic end product yet further plasticisers may need to be added. This is because if water is added to starch as the sole plasticiser, the water is able to diffuse away in the course of time, as a result of which the material becomes brittle. Various other plasticisers for starch are known, such as hydroxy compounds or polyols (such as glycol, di- and polyglycol, glycerol, erythritol, pentaerythritol, sorbitol, other sugar alcohols, gluconic acid, etc.), partial esters thereof, amide compounds (such as urea) and metal carboxylates (such as sodium lactate). The amount of other plasticiser, based on the dry starch or starch/biopolymer mixture, is preferably 8 - 75 % (m/m), more preferentially 10 - 50 % (m/m) and in particular 15 - 45 % (m/m). The percentage of plasticisers that is needed for gelatinising starch can already be reduced by adding small amounts of the present carbohydrate polymer.

Clay minerals can also be added to the mixture to be extruded. Such mixture can comprise starch or a starch/biopolymer mixture with the present carbohydrate polymer and plasticisers, one of which is water. Reference is in this context made to WO 01/68762, which document is herein incorporated by reference. The clay minerals concerned are preferably montmorillonite, saponite, hectorite and other minerals of the smectite type.

The amount of clay particles can vary from, for example, 1 - 50 % (m/m), and in particular 2 - 10 % (m/m), based on the dry weight of the starch (and any other biopolymers). The addition of clay leads to an improvement in the mechanical and gas barrier properties of 5 the end product. In addition to naturally occurring polymers, biodegradable synthetic polyesters can be added to the mixture, for example the polyesters as described in US 6,348,524, in particular polycaprolactone, polylactate, polyhydroxyacetate and polyhydroxybutyrate, polyethylene succinate, polybutylene succinate and the like, as well as copolymers and mixtures 10 thereof. The amount of polyester can, for example, be between 10 and 80 % (m/m), based on the amount of dry starch.

The polyester can be blended directly with the extrudate, but, if used, is preferably added in the course of the process, for example at a point halfway through the extrusion.

15 Depending on the application of the end product, additives such as pigments, stabilisers, processing agents, flavours and fragrances, and also anti-fouling agents or release retarders, can also be added.

The thermo mechanical treatment is preferably carried out in the form of an extrusion process in a twin-screw extruder and at temperatures of 20 70-170 °C. Preferably, the thermo mechanical treatment is carried out at a temperature of less than 115 °C, more preferably at a temperature in the range of from 80 to 100 °C. The temperatures mentioned here refer to the actual temperatures in the extruder. High shear forces during the extrusion to disrupt the starch crystal structure, such as those which are customary in 25 present day production of thermoplastic starch, have become superfluous as a result of the use of water as plasticiser and the addition of the present carbohydrate polymer. In this way, the processing of biopolymers to give a thermoplastic material becomes distinctly energy-saving and the production rate is increased at the same time. In principle, discontinuous thermo 30 mechanical treatment is also possible, but has the disadvantage of a lower productivity. The advantages of the invention are best revealed in a

continuous process. Hence, in the present invention the thermo mechanical treatment is preferably carried out continuously.

With the thermo mechanical treatment semi-finished products in the form of granulates, sheets, films or other forms are produced that can be 5 further processed. These thermoplastic products must usually be stored for at least 3 hours immediately after extrusion to reach a thermodynamically stable equilibrium, and to obtain a completely water-resistant product. Storage can best take place in a closed box or bag, but can also be carried out in an open store if the atmospheric humidity is not less than 50 % (RH). These 10 thermoplastic semi-finished products can be further processed in a known thermo mechanical manner to give shaped articles by means of injection moulding, foaming, film casting, deep drawing, film blowing, film pressing and the like.

The invention also relates to the intermediate product that can be 15 obtained by the process described above, in particular a granulate, powder, film, etc, and to the shaped end product that can be obtained from this intermediate product. The granulate of thermoplastic starch as obtained according to the invention can be processed to give hot-pressed films and further processed by means of film blowing. Other shaping steps, such as 20 injection moulding or thermoforming, can also be employed. The end product can, in particular, be a blown film, which in addition to the starch and the present carbohydrate polymer and any other biopolymers and plasticisers can contain 10-80 %, in particular 10-40 % (m/m) polyester.

The present invention therefore also relates to a granulate of 25 thermoplastic starch that comprises a carbohydrate polymer in an amount in the range of from 1 to 10 weight %, based on total thermoplastic starch, a polyol or urea as plasticiser and water, which carbohydrate polymer comprises aldehyde containing monomer units, whereby at least 1% of the aldehyde containing units comprise no more than one aldehyde group per monomer unit, 30 and the remaining aldehyde containing monomer units comprise two or more aldehyde groups per monomer unit.

The present invention further relates to a shaped starch product that comprises a carbohydrate polymer in an amount in the range of from 1 to 10 weight %, based on total thermoplastic starch, a polyol or urea as plasticer and water, which carbohydrate polymer comprises aldehyde containing monomer units, whereby at least 1 % of the aldehyde containing units comprise no more than one aldehyde group per monomer unit, and the remaining aldehyde containing monomer units comprise two or more aldehyde groups per monomer unit.

Additionally, the present invention also relates to a blown starch film that comprises a carbohydrate polymer in an amount in the range of from 1 to 10 weight %, based on total thermoplastic starch, a polyol or urea as plasticer and water, which carbohydrate polymer comprises aldehyde containing monomer units, whereby at least 1 % of the aldehyde containing units comprises no more than one aldehyde group per monomer unit, and the remaining aldehyde containing monomer units comprise two or more aldehyde groups per monomer unit.

#### Example 1

Using a Hobart N-50 mixer, 1.2 kg native potato starch (containing 15 % moisture) was mixed with 400 g MACS (mono aldehyde carboxy starch containing 10 % dialdehyde and 5 % monoaldehyde-carboxy groups [moisture content 30 %]), 250 g water and 300 g glycerol. The premix was processed using a twin-screw co-rotating extruder (L/D = 11) at 80 °C and 200 rpm. The product throughput in the extruder was around 3.3 kg/h. The extrudate was homogeneous, transparent and flexible. The degree of gelatinisation was determined using a polarisation optical microscope (POM). No granules of native starch were discernible in a POM photograph. The samples were still completely dimensionally stable after 5 hours in water (20 °C).

**Example 2 (comparison)**

Using a Hobart N-50 mixer, 0.9 kg native potato starch (containing 15 % moisture) was mixed with 250 g water and 324 g glycerol. The premix was processed using a twin-screw co-rotating extruder (L/D = 11) at 100 °C and 200 rpm. The product throughput in the extruder was at most 1.77 kg/h. The extrudate was homogeneous and flexible. The product was white/opaque because it was hardly gelatinised. The gelatinisation was determined using POM. A very large number of granules of native starch were visible in a POM photograph. After storage, the granulate is dimensionally stable in water at room temperature.

**Example 3**

Using a Hobart N-50 mixer, 1.0 kg native potato starch (containing 15 % moisture) was mixed with 400 g aldehyde starch (obtained through TEMPO mediated oxidation and containing 4 out of 100 anhydro glucose units carboxylic acids and 10 aldehyde groups out of 100 anhydro glucose units aldehyde and had a moisture content of 8 %), 250 g water and 250 g glycerol. The premix was processed using a twin-screw co-rotating extruder (L/D = 11) at 80 °C and 200 rpm. The product throughput in the extruder was at most 3.0 kg/h. The extrudate was homogeneous, transparent and flexible. The extrudate was completely gelatinised and 100 % amorphous. The degree of gelatinisation was determined using a polarisation optical microscope (POM). No granules of native starch were discernible in a POM photograph. The samples were still completely dimensionally stable after 5 hours in water (20 °C).

**Example 4**

Using a Hobart N-50 mixer, 1.0 kg native potato starch (containing 15 % moisture) was mixed with 500 g aldehyde starch (obtained via substitution using allylglycidyl ether according to the method described in WO 01/87986

and subsequent ozonolysis of the double bonds yielding modified polymers that contained on average 6 aldehyde functionalities per 100 anhydro glucose units and had a moisture content of 15 %), 200 g water and 250 g glycerol. The premix was processed using a twin-screw co-rotating extruder (L/D = 11) at 80 5 °C and 200 rpm. The product throughput in the extruder around 3.1 kg/h. The extrudate is homogeneous, transparent and flexible. The extrudate was completely gelatinised and 100 % amorphous. The degree of gelatinisation was determined using a polarisation optical microscope (POM). No granules of native starch were discernible in a POM photograph. The samples were still 10 completely dimensionally stable after 5 hours in water (20 °C).

Claims

1. A process for gelatinising starch and/or a starch derivative by subjecting starch and/or a starch derivative in the presence of a carbohydrate polymer to a thermo mechanical treatment, which carbohydrate polymer comprises aldehyde containing monomer units, whereby at least 1 % of the aldehyde containing monomer units comprise no more than one aldehyde group per monomer unit, and the remaining aldehyde containing monomer units comprise two or more aldehyde groups per monomer unit.  
5
2. A process according to claim 1, wherein at least 10 % of the aldehyde containing monomer units comprise one aldehyde group per monomer unit.  
10
3. A process according to claim 2, wherein at least 20 % of the aldehyde containing monomer units comprise one aldehyde group per monomer unit.  
15
4. A process according to any one of claims 1-3, wherein the aldehyde containing monomer units in the carbohydrate polymer comprise a non-cleaved vicinal diol system.  
20
5. A process according to any one of claims 1-4, wherein the carbohydrate polymer comprises  $\alpha$ -1,4-glucans (the "starch family"),  $\beta$ -1,4-glucans (cellulose), glucomannans and galactomannans (guar and locust bean gum), arabinoxylans and xylans (hemicellulose) and  $\beta$ -2,1 and  $\beta$ -2,6-fructans (inulin and levan)  
25
6. A process according to claim 5, wherein the carbohydrate polymer comprises starch, cellulose, hemi-cellulose, and/or galactomannans.

7. A process according to any one of claims 1-6, wherein the one aldehyde group is introduced in the monomer unit at the C-6 position.

8. A process according to any one of claims 1-6, wherein the one aldehyde group is introduced in the monomer unit by means of protected aldehydes (acetals) or substituted unsaturated functionalities followed by oxidation of through hindered nitroxyl mediated oxidation.

9. A process according to any one of claims 1-8, wherein the carbohydrate polymer is present in an amount of from 1 to 15 weight %, based on the total weight of the starch and the carbohydrate polymer.

10. A process according to any one of claims 1-9, wherein the thermo mechanical treatment is carried out at a temperature of less than 115 °C.

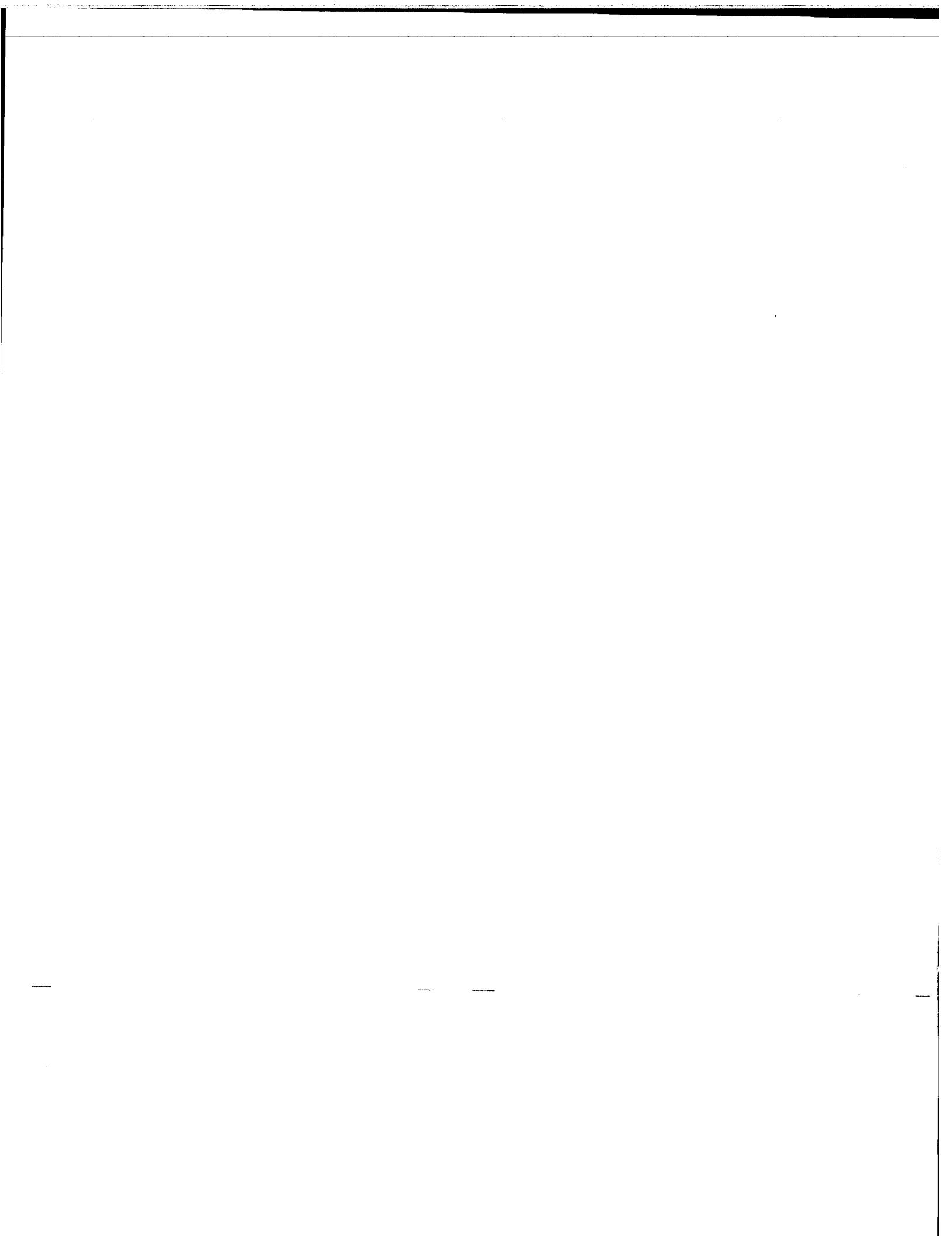
11. A process according to any one of claims 1-10, wherein the thermo mechanical treatment is carried out continuously.

12. A granulate of thermoplastic starch that comprises a carbohydrate polymer in an amount in the range of from 1 to 10 weight %, based on total thermoplastic starch, a polyol or urea as plasticer and water, which carbohydrate polymer comprises aldehyde containing monomer units, whereby at least 1 % of the aldehyde containing units comprise no more than one aldehyde group per monomer unit, and the remaining aldehyde containing monomer units comprise two or more aldehyde groups per monomer unit.

13. A shaped starch product that comprises a carbohydrate polymer in an amount in the range of from 1 to 10 weight %, based on total thermoplastic starch, a polyol or urea as plasticer and water, which carbohydrate polymer comprises aldehyde containing monomer units, whereby at least 1 % of the

aldehyde containing units comprise no more than one aldehyde group per monomer unit, and the remaining aldehyde containing monomer units comprise two or more aldehyde groups per monomer unit.

5 14. A blown starch film that comprises a carbohydrate polymer in an amount in the range of from 1 to 10 weight %, based on total thermoplastic starch, a polyol or urea as plasticer and water, which carbohydrate polymer comprises aldehyde containing monomer units, whereby at least 1 % of the aldehyde containing units comprise no more than one aldehyde group per 10 monomer unit, and the remaining aldehyde containing monomer units comprise two or more aldehyde groups per monomer unit.



Abstract

The invention provides a process wherein starch and/or a starch derivative can be gelatinised more efficiently by means a thermo mechanical treatment, when a carbohydrate polymer is used comprising aldehyde containing monomer units which comprise one aldehyde group only. With this process a granulate or other semi-finished product can be obtained that can be shaped to produce an article that has excellent dimensional stability in water. The invention further provides a granulate, a shaped starch product or a blown starch film comprising such a carbonate polymer.

